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NATIONAL INVENTORY OF SOURCES AND EMISSIONS: ARSENIC-1968

W. E. Davis, and Associates

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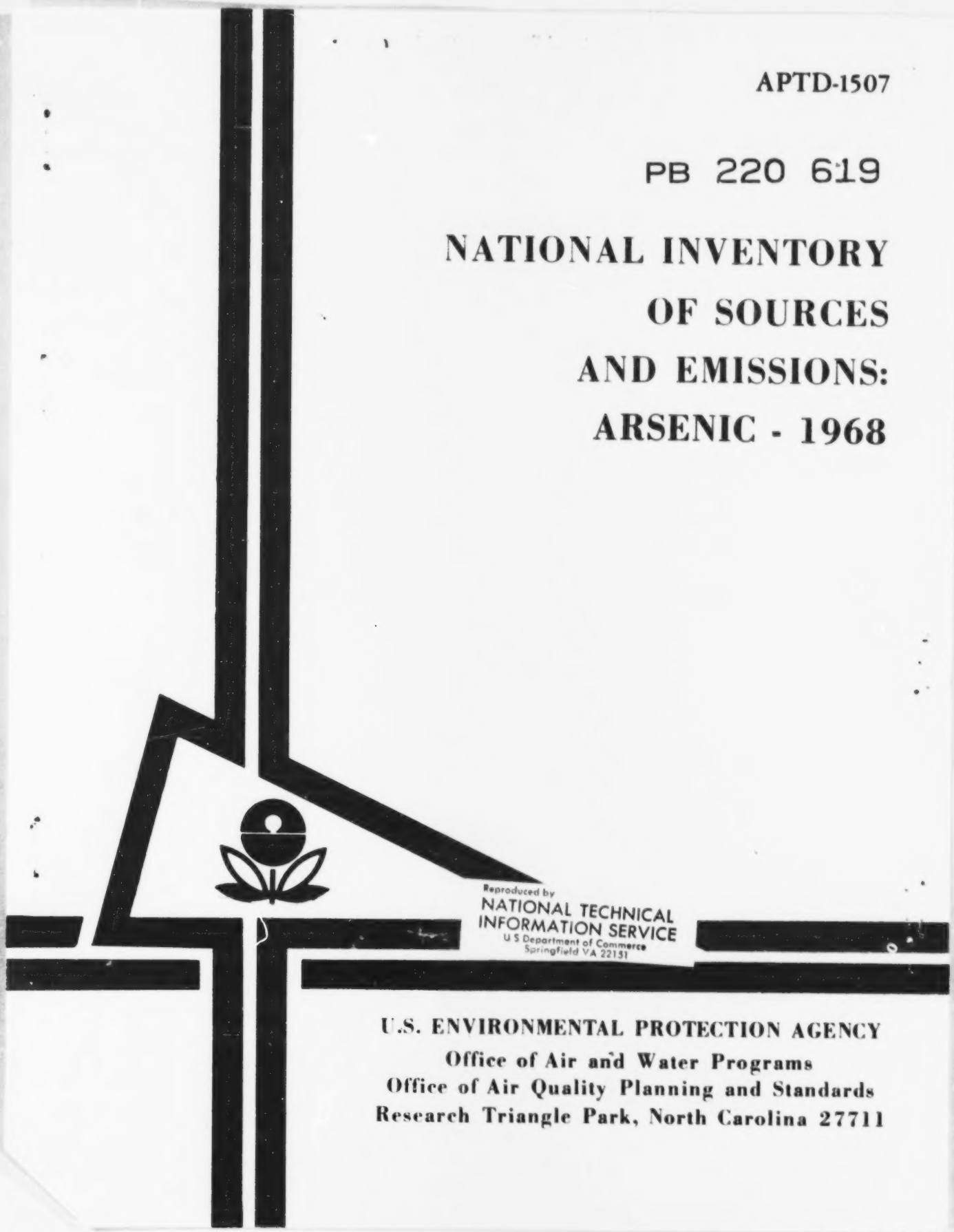

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Research Triangle Park, North Carolina 27711

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NATIONAL INVENTORY OF SOURCES AND EMISSIONS: ARSENIC - 1968

by

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Contract No. CPA-70-128

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Prepared for

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Office of Air and Water Programs
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May 1971

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Publication No. APTD-1507

PREFACE

This report was prepared by W. E. Davis & Associates pursuant to Contract No. CPA 70-128 with the Environmental Protection Agency, Air Pollution Control Office.

The inventory of atmospheric emissions has been prepared to provide reliable information regarding the nature, magnitude, and extent of the emissions of arsenic in the United States for the year 1968.

Background information concerning the basic characteristics of the arsenic industry has been assembled and included. Process descriptions are given, but they are brief, and are limited to the areas that are closely related to existing or potential atmospheric emissions of the pollutant.

Due to the limitation of time and funds allotted for the study, the plan was to personally contact about twenty to thirty percent of the companies in each major emission source group to obtain the desired information. It was known that published data concerning emissions of the pollutant was virtually nonexistent, and numerous contacts with industry during the study ascertained that atmospheric emissions were not a matter of record.

The arsenic emissions and emission factors presented herein are based on the summation of information obtained from the one processing company that produced arsenic during 1968, the copper, lead, and zinc smelters, and the reprocessing companies that handle about fifty percent of the arsenic consumed in the United States. Arsenic emissions and emission factors are considered to be reasonably accurate.

ACKNOWLEDGEMENTS

This was an industry oriented study and the authors express their appreciation to the many companies and individuals that contributed information related to the atmospheric emissions of arsenic.

We wish to express our gratitude for the assistance of the various societies and associations, and to the many branches of the Federal and State Governments.

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SUMMARY

The production and use of arsenic in the United States has been traced and charted for the year 1968. The total consumption of 28,000 tons was used as follows: 72 percent by imports (20,000 tons), and 28 percent by domestic producers (8,000 tons).

During the year emissions from metallurgical processing plants of the primary producers of copper, lead, and zinc were 4,466 tons, and those due to the use of pesticides were 3,270 tons. These two emission sources combined account for 82 percent of the 9,415 tons total emissions.

Arsenic emissions to the atmosphere can be reduced. A decrease in imports, coupled with an increase in domestic production, would result in less emissions. Many nonferrous smelters currently process ores that contain significant quantities of arsenic. With a sufficient economic incentive, some would recover the element rather than treating it as an unwanted by-product.

Emission estimates for processing and reprocessing operations are considered to be reasonably accurate. They are based on estimates obtained through personal contact with the processing and reprocessing companies, and on engineering calculations supported by data covering smelter gas flow rates and temperatures.

EMISSIONS BY SOURCE
1968

Source Category	Source Group	Short Tons	
Mining			2
Metallurgical Processing			4,466
	Copper Smelters	2,700	
	Zinc Smelters	1,390	
	Lead Smelters	376	
Reprocessing			837
	Agricultural	196	
	Glass	638	
	Wood Preservatives	N	
	Nonferrous Alloys	N	
	Other	3	
Consumptive Uses			4,013
	Agricultural	3,270	
	Coal	743	
	Oil	NA	
Incineration and Other Disposal			97
	Cast Iron	97	
TOTAL			9,415

N - Negligible (less than 1 ton)

NA - Not Available

EMISSIONS BY REGION

	Number of Smelters	Short Tons
Region No. 1	22	3,829
Region No. 2	4	1,317
Region No. 3	8	2,313
Region No. 4	2	1,020
Undistributed		936
TOTAL		9,415

MAP OF EMISSION REGIONS
REGION 1
REGION 2
REGION 3
REGION 4
PLANT LOCATIONS
Arsenic
Copper
Lead
Zinc

Figure 1

EMISSION FACTORS

Mining	0.2 lb/ton of arsenic in ore
Metallurgical Processing	
Copper Smelters	4.9 lb/ton of copper
Zinc Smelters	1.3 lb/ton of zinc
Lead Smelters	0.8 lb/ton of lead
Reprocessing	
Agricultural	20 lb/ton of arsenic used
Glass	232 lb/ton of arsenic used
Other	3 lb/ton of arsenic used
Consumptive Uses	
Agricultural	336.0 lb/ton of arsenic used
Cotton Gin	3.5 lb/1,000 bales of cotton ginned
Burning Cotton Gin Trash	17.0 lb/1,000 bales of cotton ginned
Coal	2.9 lb/1,000 tons of coal burned
Incineration and Other Disposal	
Cast Iron	11 lb/1,000 tons of metal charged

SOURCES OF ARSENIC

Arsenic is not an abundant element, but it is widely distributed in the earth's crust. Traces of it can be found almost everywhere. It is present in sea water, in coal deposits, and in virgin soils as well as in various ores. The most extensive occurence is with copper, lead, cobalt, nickel, iron, gold, and silver.

Arsenic is generally regarded as a contaminant in the ore and must be removed during smelting and refining in order to improve the quality of the metal. During 1968 it was produced commercially only at one location in the United States. At many other locations it was an unwanted by-product. One of the problems facing the mining industry has been the disposal of large quantities of crude arsenic produced while purifying other metals.

In the United States arsenic occurs in many ores of ferrous metals and nonferrous base metals. Gold and silver ores are often associated with arsenic and contain large reserves of arsenic [1]. Copper ores in Arizona usually contain a small amount of arsenic, while ores in many other western states contain considerably more. Often lead, copper, and gold ores contain as

---

1- Mineral Facts and Problems; U. S. Bureau of Mines; 1965.

much as 2 or 3 percent arsenic and in a few instances, as much as 10 or 12 percent.

Copper, lead, and zinc ores and concentrates which are imported and processed in the United States also contain arsenic.

ARSENIC

MATERIAL FLOW CHART - 1968

Short Tons - Arsenic (As)

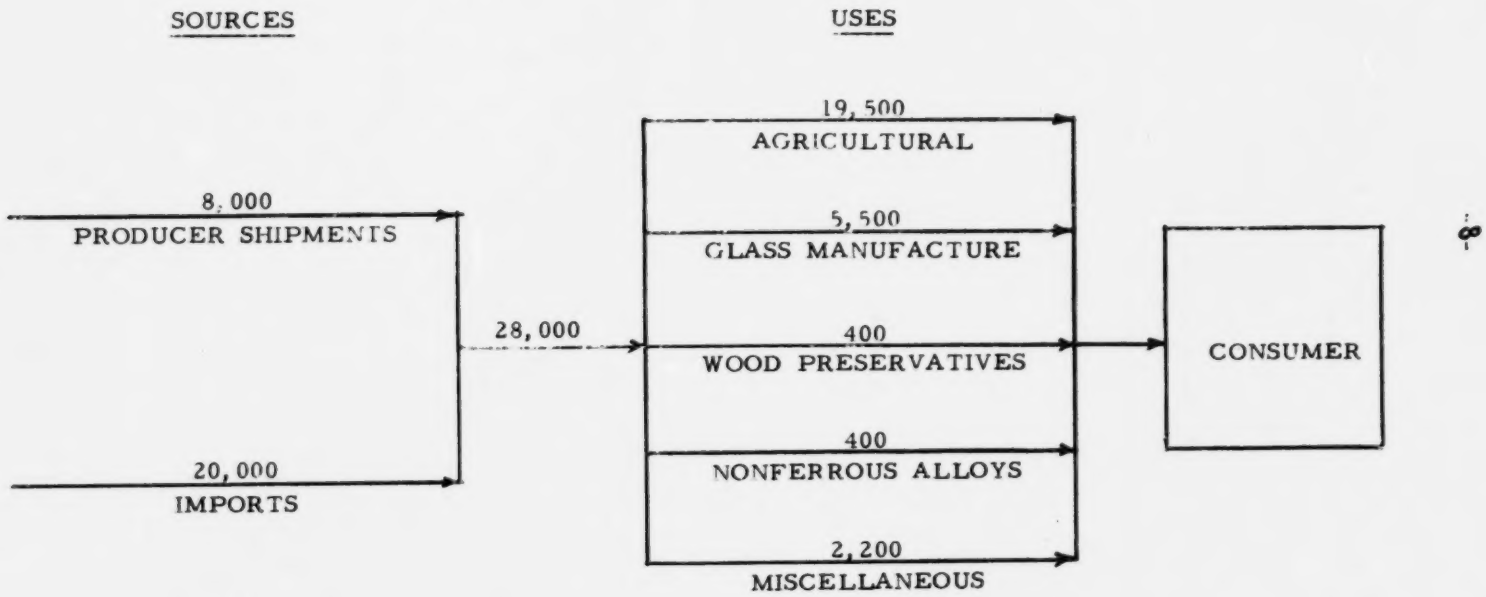

Figure II

MATERIAL FLOW

MINING AND PROCESSING

During 1968 arsenic was produced commercially in the United States only at the American Smelting and Refining Company copper smelter in Tacoma, Washington [1]. It was produced as a by-product of copper smelting not only from copper ores and concentrates, but also from speiss, flue dust, and sludges received from other smelting plants.

Arsenic produced domestically and shipped from producer stocks during 1968 totaled about 8,000 tons (As content) [2]. It was produced as arsenic trioxide or arsenious oxide (As_2O_3), which is often referred to as white arsenic.

1- Minerals Yearbook; Bureau of Mines; 1968.

2- An estimate based on information in the Bureau of Mines Minerals Yearbooks, 1958 through 1968.

ARSENIC IMPORTS

During 1968 arsenic imports totaled 20,000 tons (As content), consisting principally of white arsenic and metallic arsenic [1]. About 37 percent of the white arsenic was imported from Sweden, 29 percent from Mexico, and 25 percent from France. Sweden was the major supplier of metallic arsenic.

1- Minerals Yearbook; Bureau of Mines; 1968.

CONSUMPTIVE USES

The apparent consumption of arsenic in the United States during 1968 has been estimated at 28,000 tons (As content) [1]/.

Arsenic is produced principally in the oxide form (white arsenic) and used extensively in the manufacture of calcium arsenate and lead arsenate; smaller quantities are also used in sodium arsenite, sodium arsenate, arsenic acid, and other compounds. Arsenic is used primarily for its toxic effect on plants and insects. It is used to a lesser extent in glassmaking, nonferrous alloys, wood preservatives, and for numerous miscellaneous purposes.

AGRICULTURAL

During recent years about 70 to 80 percent of the arsenic consumed in the United States has been used in the manufacture of pesticides, including herbicides, defoliants, fungicides, and insecticides. Various forms of arsenic used in these materials include: calcium and lead arsenate, calcium and zinc arsenite, arsenic acid, cacodylic acid, and arsenic trioxide (white arsenic).

1- Estimated tonnage is based on imports reported in the Bureau of Mines Minerals Yearbook, 1968, plus estimated producer shipments.

Herbicides are used principally to control weed growth. Calcium, sodium and zinc arsenites, plus some organic arsenicals, are used for this purpose and are usually applied in the form of a water solution.

The major use of defoliants and desiccants in the United States is for treatment of cotton prior to machine picking. The product most used for this purpose is arsenic acid. Another defoliant is cacodylic acid, but due to higher cost it is consumed in smaller quantities.

Another important area for use of arsenic is in insecticides. The most common arsenate products used for this purpose are calcium and lead arsenate. These may be used either as sprays or dusting materials which are applied to orchards, gardens, berries, ornamentals, and field crops in a form that will not injure plants, but chewing insects are destroyed when they eat leaves which have been treated with the arsenic-containing sprays or dusting preparations.

It is estimated that 19,500 tons of arsenic were used for agricultural purposes in the United States during 1968 [1].

1- Private communication with the U. S. Bureau of Mines, Washington, D. C.

GLASS MANUFACTURE

Arsenic trioxide (As_2O_3), arsenic hemiselenide (As_2Se), arsenic pentoxide (As_2O_5), and arsenic trisulfide (As_2S_3) are used in the manufacture of glass.

Approximately 5,500 tons of arsenic were used in the manufacture of glass during 1968 [1].

WOOD PRESERVATIVES

Various arsenic compounds are used extensively as wood preservatives either alone, or mixed with other substances. Such compounds include arsenic trioxide, chemonite, ammoniacal copper arsenite, and chromated copper arsenate.

Arsenic used in wood preservatives in the United States during 1968 totaled approximately 400 tons [2].

NONFERROUS ALLOYS

Arsenic in small amounts is added to some copper and lead alloys to improve corrosion and erosion resistance, raise the annealing temperature, change the surface tension, harden the

---

1- Private communication with the U. S. Bureau of Mines, Washington, D. C.

2- Minerals Yearbook; Bureau of Mines; 1968.

alloy, or otherwise alter the characteristics of the metal to make it suitable for certain special purposes.

It is estimated that 400 tons of arsenic were used in nonferrous alloys in the United States during 1968 [1].

OTHER

Small quantities of arsenic are used in cattle and sheep dips, pyrotechnics, pigments, semiconductors, poultry feed additives, pharmaceuticals, and in treating hides and skins.

Sodium arsenite is the active ingredient in certain cattle and sheep dips. It is also used to a limited extent for termite control.

Arsenic disulfide and arsenic trisulfide are found in nature but ordinarily are made artificially. They are used in paint pigments and pyrotechnics. Arsenic disulfide is also used as a depilatory in tanning. Arsenic pentasulfide has a limited use in paint pigments and pyrotechnics.

There is limited demand for arsenic of extremely high purity (99.999%) for use as a semiconductor.

1- Private communication with the U. S. Bureau of Mines, Washington, D. C.

In the past arsenic compounds have been used rather extensively in medicine, but today the applications are limited. Less than one percent of the annual arsenic supply is used in pharmaceutical preparations.

During 1968 the estimated uses of arsenic in this category totaled 2,200 tons.

EMISSIONS

MINING AND PROCESSING

Since no ore in the United States is mined solely for the recovery of arsenic, the emissions to the atmosphere resulting from mining operations are those that occur during the mining and concentration of copper, lead, and other ores that contain arsenic.

Regardless of the type of mine (underground or open-pit), the mining operations are basically the same: ore removal, ore handling, crushing, grinding, and concentration. During many of the operations the ore is wet and emissions to the atmosphere are virtually nonexistent. The principal emission appears to be that due to wind loss from tailings.

Arsenic emissions to the atmosphere from sources of mining are estimated at 0.2 pounds per ton of arsenic handled. This gives a total figure of approximately 2 tons of arsenic emitted to the atmosphere during 1968.

METALLURGICAL PROCESSING

During 1968 arsenic for the commercial market was produced at only one location in the United States. It was recovered as arsenic trioxide from dusts and residues as well as from foreign and domestic copper ores and concentrates.

Since most of the arsenic produced is in the form of arsenic trioxide (As_2O_3) as a by-product of the smelting of other metals, the production of arsenic is closely associated with the recovery and treatment of arsenic-bearing flue dusts. As arsenic trioxide is volatilized during the smelting of copper, lead, zinc, and other metals, it is concentrated in the flue dust. The crude flue dust carrying up to 30 percent arsenic trioxide also contains oxides of copper or lead, and perhaps other metals such as antimony, zinc, and cadmium.

The crude flue dust recovered during the smelting operation is further refined by mixing it with a small quantity of pyrite or galena concentrate prior to roasting. The pyrite or galena prevents the formation of arsenites during roasting, and produces a clinkered residue suitable for return to the process for recovery of other metals. The gases from roasting are passed through a series of brick chambers or kitchens, in which the

temperature varies from 430 F in the first, to 210 F or less in the last. As the gases cool, arsenic trioxide condenses as a crude white arsenic, 90 to 95 percent pure. Much of the product is used in this form without further refinement.

If higher purity is required, the refining is usually carried out in a reverberatory furnace at a roasting temperature of about 1,000 F. The vapors first pass through a settling chamber and then through a series of kitchens. In the settling chamber, the temperature is maintained above the condensation temperature of the trioxide. In the kitchens near the furnace a black, amorphous mass is condensed which contains about 95 percent arsenic trioxide. This product is reprocessed. The bulk of the trioxide is condensed in the other kitchens at temperatures ranging from 250 to 360 F, and most of the dust which exits from the kitchens is caught in a baghouse. Some of the arsenic escapes; all that is in the vapor phase, plus a relatively small amount of the dust.

A flowsheet (Figure III) shows the basic steps for production of arsenic trioxide at a copper smelter [1].

1- Kirk, R. E. and Othmer, D. F.; Encyclopedia of Chemical Technology; 2nd Ed.; Interscience Publishers; New York, N. Y.; 1963.

ARSENIC FLOW SHEET
COPPER SMELTER

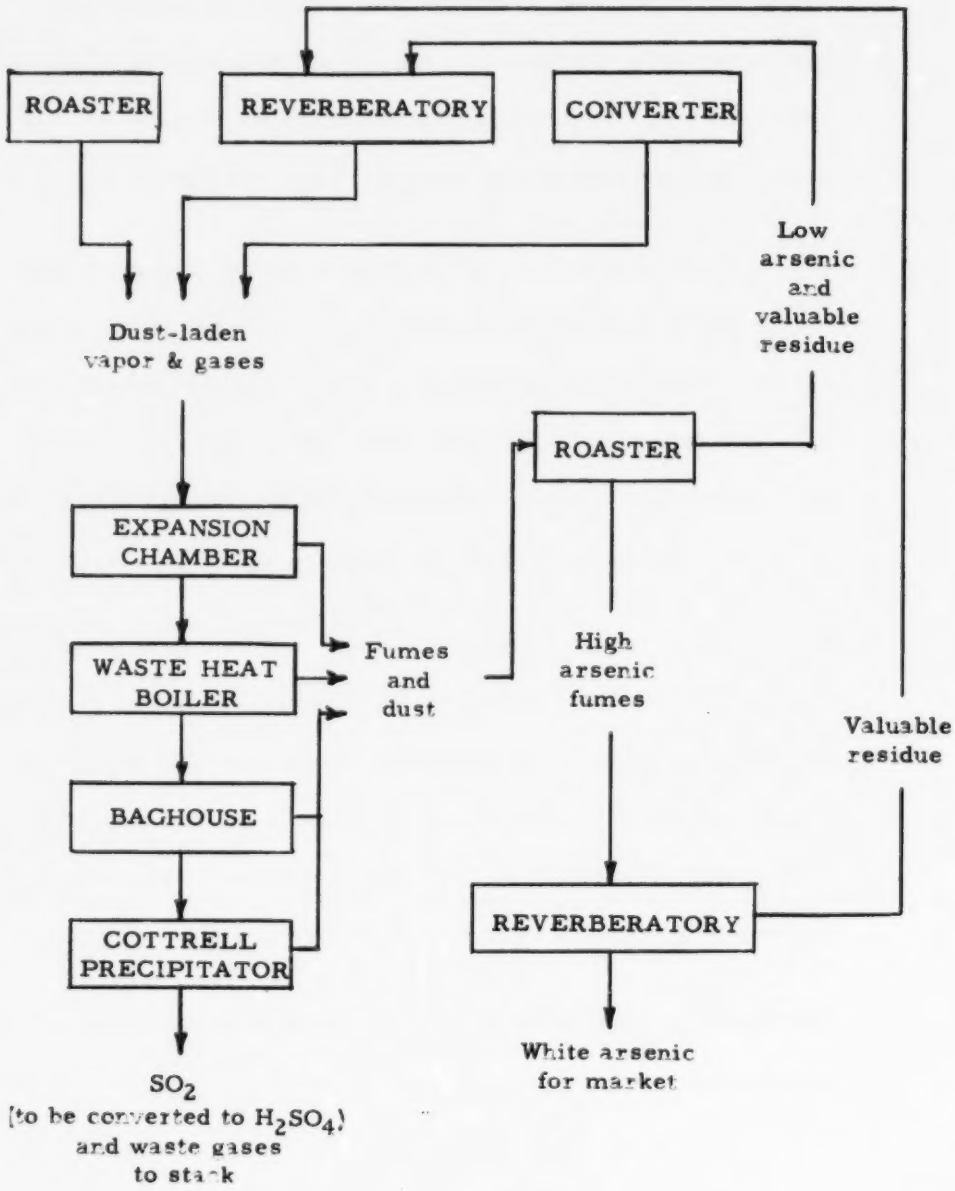

Figure III

One of the big problems facing the mining industry has been the disposal of large quantities of arsenic contained in various ores mined and processed. The quantity of arsenic available has greatly exceeded the demand; therefore, most smelters have not attempted to produce arsenic for the commercial market. There is no economic incentive to remove it from the flue gas.

At many smelters no attempt is made to control arsenic emissions, but at others some method of control is required. If the arsenic content of the ore is low, as it is in copper ores in Arizona, likely there will be no control. The arsenic retained in the copper product will be within commercial limits and that discharged in the slag and to the atmosphere will be relatively minor.

If the arsenic content of the ore is high, some method of control is essential. In some instances the flue dust containing high concentrations of arsenic is removed from the smelting process at regular intervals to prevent excessive arsenic build-up in the system and in the product. Sometimes the flue dust is sold to a smelter that produces arsenic, and sometimes it is dumped.

The following six examples demonstrate arsenic problems in mining ore.

1 - The Boliden Mining Company in Sweden is one of the world's largest producers of arsenic. Arsenical gold ore containing 10 percent or more of arsenic is processed; the arsenic output is sufficient to supply a large share of the world demand. At the beginning of the Boliden operation it was realized that the arsenic output would be far in excess of demand and that disposal would be a major problem. First the excess crude arsenic was mixed with cement, made into blocks, and dumped far out at sea. This method of disposal proved to be rather expensive and an alternate method was devised. A large concrete storehouse was erected in 1931 and the crude arsenic was stored close at hand. Since that time additional storehouses have been constructed as required.

2 - At other locations the lack of adequate control has resulted in harmful emissions to the atmosphere. During the years 1903 to 1905 large quantities of arsenic were emitted from a copper smelter in Montana. The emission rate was reported as 59,270 lb/day when the ore processed was 10,000 tons/day. Large numbers of animals were killed up to fifteen miles from the smelter due to eating plants contaminated with arsenic

trioxide [1,2,3].

3 - In Nevada a gold smelter was reopened in 1962, but within five months it became apparent that the electrostatic precipitator equipment was inadequate. Large quantities of arsenic trioxide escaped into the atmosphere. If the dust-collecting system had operated at 90 percent efficiency as intended, about 15,000 tons of crude arsenic trioxide would have been collected each year. The analysis of dust samples from the area near the plant are shown in Table I.

4 - After an air pollution episode at a copper mine in northern Chile, samples of ore and dust were analyzed and reported as shown in Table II.

5 - According to a report concerning another copper smelter in South America, the arsenic in the ore is recovered as crude arsenic trioxide and dumped in the open on company property near

---

1- Harkins, W. D. and Swain, R. E.; "The Determination of Arsenic and Other Solids in Smelter Smoke"; J. Am. Chem. Soc.; 29; p. 970; 1907.

2- Harkins, W. D. and Swain, R. E.; "The Chronic Arsenical Poisoning of Herbivorous Animals"; J. Am. Chem. Soc.; 30; p. 928; 1908.

3- Haywood, J. K.; "Injury to Vegetation and Animal Life by Smelter Fumes"; J. Am. Chem. Soc.; 29; p. 998; 1907.

TABLE I

ARSENIC CONTAMINATION IN
A WESTERN MINING COMMUNITY [1]

Sample	Site	Arsenic Concentration
Flue Dust	Base of stack	44.0%
Roof Dust	Shed near office	4.4%
Dust	Area near drying mill	2.7%
Dust	Roaster area	3.1%
Dust	Sulfide-ore feed	1.23%

1- Birmingham, D. J., Key, M. M., Holaday, D. A., and Perone, V. B.; "An Outbreak of Arsenical Dermatosis in a Mining Community"; Arch. Dermatol.; 91; p. 457; 1965.

TABLE II

CONCENTRATION OF ARSENIC
NEAR A COPPER MINE IN NORTHERN CHILE [1]

Sample	Arsenic Concentration
Mineral (ore)	0.054%
Concentrated Ore	1.64%
Calcined Ore	0.30%
Dust from Electrostatic Precipitator	10.36%
Dust from Stack	16.64%

1- Oyarguren, H. and Parez, E.; "Poisoning of Industrial Origin in a Community"; Arch. Environ. Health 13; p. 185; 1966.

the smelter. Based on material balance data and stack sample analyses, the arsenic emission to the atmosphere is slightly more than 8 percent. The concentrates contain 12 to 13 percent copper and 2.7 percent arsenic. The flue dust in the stack averages about 25 percent arsenic [1]/.

6 - One zinc smelter in the United States reported the average arsenic content of zinc concentrates as approximately 0.075 percent. The estimated arsenic output from the smelter is as follows.

ARSENIC OUTPUT FROM A
ZINC SMELTER IN THE UNITED STATES

Output	Percent
In Products	0.3
In Saleable Residues	17.6
In Dust	1.5
To the Atmosphere	80.6
TOTAL	100.0

Arsenic emissions from copper, lead, and zinc smelters vary considerably from plant to plant and from year to year. Arsenic emission factors for copper smelters range from one

1- Private communication; industrial source.

pound to 53 pounds per ton of copper, and the average for 1968 was 4.9. The average emission factor for zinc smelters was 1.3 pounds per ton of zinc, and for lead plants 0.8 was the average.

Emissions from a few of the processing plants that did not produce arsenic were far greater than those from the one plant that did produce for the commercial market. Undoubtedly, more arsenic would be produced and less emitted to the atmosphere if there were a greater incentive for smelters to recover the element.

During 1968 estimated arsenic emissions to the atmosphere due to metallurgical processing of arsenic-bearing ores totaled 4,466 tons. The emission estimates are based on material balance and stack sampling data obtained from industrial sources.

REPROCESSING

During 1968 about 70 percent of the arsenic consumed in the United States was used for agricultural purposes, and nearly 20 percent was used in glassmaking. The remaining 10 percent was used for various purposes including wood preservatives, nonferrous alloys, animal dips, paints, pyrotechnics, poultry feeds, and other products.

AGRICULTURAL

The principal use of white arsenic is in the manufacture of the arsenical pesticides. Some of the compounds are listed below.

AGRICULTURAL PESTICIDE COMPOUNDS

Sodium arsenate	Cacodylic acid
Lead arsenate	Calcium arsenite
Calcium arsenate	Zinc arsenite
Zinc arsenate	Sodium arsenite
Arsenic acid	Disodium methyl arsenate

All these compounds are produced from arsenic trioxide and the manufacturing process is relatively simple. Arsenic acid is produced by reacting arsenic trioxide with nitric acid. Calcium arsenate is produced by reacting arsenic acid with lime, lead

arsenate by reacting arsenic acid with litharge (lead oxide). Arsenic trioxide reacted with sodium hydroxide produces sodium arsenite.

Since the production of arsenic compounds is simple, many of the manufacturers of pestidices commence their operation with the purchase of arsenic trioxide and other basic materials. They prepare the arsenic compounds, then formulate and package the pesticides. Some of the manufacturers are large, others are small, and size seems to be the most important factor governing the general type of equipment used to prepare the compounds and pesticides. When the operation is small, arsenic trioxide is usually received in casks or barrels and unloaded by hand. Reactions are often carried out in closed vessels. The principal problem from the standpoint of atmospheric emissions stems from dusting during handling of the materials.

Many of the large manufacturers are prepared to handle bulk materials. At one location arsenic trioxide is received in railroad cars and dumped directly below into a receiving tank where it is reacted with nitric acid to produce arsenic acid.

Reports from pesticide manufacturers indicate that arsenic losses are small. None of the reactions result in significant

vapor emissions to the atmosphere and most of the dusting situations are usually handled by air pollution control systems consisting of hoods, ducts, exhaust fans, and baghouses. The dusts handled are in the 0.5 to 10 micron range.

Manufacturers state their material records indicate no detectable losses of arsenic during processing; however, it is evident there is a slight atmospheric emission which is estimated at 20 pounds per ton of arsenic processed.

During 1968 arsenic emissions to the atmosphere due to the manufacture of pesticides totaled 196 tons.

GLASS MANUFACTURE

Arsenic is used in nearly all types of glass. It aids in the removal of bubbles during manufacturing and acts as a stabilizer of selenium in decolorizing crystal glasses.

The proportion of arsenic used is very small, seldom as much as 10 pounds per ton of glass and usually not more than 2 pounds per ton. In window glass the amount used generally ranges from 1/4 pound to 5 pounds per ton [1].

1- Tooley, F. V.; Handbook of Glass Manufacture; Ogden Publishing Company; New York, N. Y.; 1953.

Of the five major types of glass produced commercially, soda-lime glass is the most widely used. It is well suited for window glass, plate glass, containers, electric light bulbs, and many other inexpensive articles. It accounts for about 90 percent of all glass production and is produced on a massive scale in large, direct-fired, regenerative furnaces that operate continuously.

Glass furnaces are usually directly fired with oil or natural gas and heat is reclaimed in checkerwork regenerators. Raw materials are charged at one end of the furnace and molten glass is pulled from the other end. Glass temperatures are as high as 2,700 F in the furnace, but usually near 2,200 F at the discharge.

There are two principal sources of particulate matter in the exhaust gases: raw materials entrained in combustion gases, and materials from the melt. Particulates expelled from the furnace are the result of many physical and chemical reactions that occur during melting. The reactions are so complex that predictions of losses cannot be based on temperature and vapor pressure data alone. One significant factor affecting the quantity of particulates is the production rate. As the production rate of the furnace is increased, the particulates also increase in quantity.

The people in the glass industry that were contacted during this study provided general information concerning glassmaking, the use of arsenic, methods of operation, and the use of air pollution control equipment, but they could not provide specific data regarding arsenic emissions to the atmosphere. Stack tests were not available showing the arsenic content of the exhaust gases, and material balance records were not sufficiently accurate concerning the minor constituents of the melt.

Particulate emissions average about 2 pounds per ton of glass produced based on good operation [1]/ and the arsenic trioxide content of the particulate has been reported as 7.71 percent [2]/. Based on the following, the emission factor for arsenic is 232 pounds per ton of arsenic used in the manufacture of glass.

1- Duprey, R. L.; Compilation of Air Pollutant Emission Factors Public Health Service Publication No. 999-AP-42; 1968.

2- Air Pollution Engineering Manual; Public Health Service Publication No. 999-AP-40; Table 212; 1968.

ARSENIC EMISSION DATA
GLASS MANUFACTURE

Particulate emission (lb/ton of glass)	- 2
Arsenic trioxide content of particulate (percent)	- 7.71
Arsenic content of arsenic trioxide (percent)	- 76
Arsenic used in glass (lb/ton of glass)	- 1
Total arsenic in glass (tons) 1968	- 5,500

During 1968 arsenic emissions to the atmosphere resulting from the manufacture of glass totaled 638 tons.

WOOD PRESERVATIVES

Wood preservatives that contain arsenic compounds have been used during the past thirty or forty years for the treatment of telephone poles, mine timbers, and other wood materials. Wolman salts and Osmosalts are wood preservatives that contain about 25 percent sodium arsenate. Bolidensalt BIS, a zinc-chromium arsenate, contains 20 percent arsenic acid and 21 percent sodium arsenate. Bolidensalt BIS Copperized also contains 20 percent arsenic acid and 21 percent sodium arsenate. Bolidensalt K33, a nonionic copper-chromium arsenate, contains 42 percent arsenic acid.

These compounds are used in solution and arsenic emissions to

the atmosphere that occur are principally those resulting from handling the dry materials during the initial processing steps. People in industry that were contacted regarding the manufacture and use of wood preservatives stated that there are no detectable emissions of arsenic during processing.

During 1968 arsenic emissions to the atmosphere resulting from the manufacture of wood preservatives are considered to be negligible.

NONFERROUS ALLOYS

Arsenic occurs naturally in many copper ores and may be permitted to remain after the refining process in concentrations of about 0.3 percent. Sometimes the element is added intentionally in amounts up to 0.5 percent and marketed under the name of "arsenical copper".

One use of arsenical copper is in building automobile radiators and other copper units that are soldered together. Since the annealing temperature of the alloy is higher than the soldering temperature, loss of strength is negligible. Another use is in heat exchangers and condenser tubes.

Arsenic is also found in many lead ores and is used in small amounts in certain lead alloys. Small additions of arsenic will

harden lead and change its surface tension. Two of the best known uses for arsenical lead are in the manufacture of batteries and munitions. One munitions manufacturer reports the use of two types of antimonial arsenical lead; type A containing 2 to 2-1/2 percent arsenic, and type B containing 1.15 to 1.25 percent arsenic. The two types are melted together to obtain the desired characteristics. For use in batteries arsenic is added principally to form hard lead which is used for battery grids, posts, and cable sheathing.

Arsenic is also used as an alloying material to produce arsenical lead babbits. This babbit is hard with a fine uniform structure that resists fatigue and is used in internal combustion engines where relatively high temperatures are encountered.

Arsenic may be added in small quantities to brass to prevent dezincification and minimize season cracking.

Alloying and melting operations cause some emissions, but manufacturers claim there is no need for special air pollution control equipment. According to the information obtained from industry, arsenic emissions to the atmosphere are approximately one pound per ton of arsenic processed.

During 1968 atmospheric emissions due to the processing of arsenic alloys were less than 1/4 ton, and are considered negligible.

OTHER

As stated elsewhere in this report sodium arsenate, arsenic disulfide, arsenic trisulfide, and arsenic pentasulfide are used in paint pigments, pyrotechnics, cattle and sheep dips, pharmaceuticals, poultry feed additives, and other miscellaneous products. A small amount of high-purity arsenic is used in semiconductors.

Some semiconductor compounds are formed by alloying arsenic with aluminum, gallium, and indium. Gallium arsenide is used in the production of tunnel and varactor diodes, transistors, solar cells, and experimental lasers. Indium arsenide also is used to produce experimental lasers as well as Hall-effect and infrared devices. A minute amount of arsenic is used in some germanium and silicon devices. Some low-melting glasses containing high-purity arsenic are useful in semiconductor and infrared applications.

Information obtained from industrial sources varies considerably regarding arsenic emissions to the atmosphere; however, all agree that the principal emission is due to handling of dry

arsenic compounds. Average emissions are estimated at 3 pounds per ton of arsenic processed.

During 1968 arsenic used in reprocessing miscellaneous products totaled 2,200 tons; atmospheric emissions were an estimated 3.3 tons.

CONSUMPTIVE USES

Household and commercial products contain arsenic, even though it is not purposely added in the manufacturing process. Arsenic in detergents is one example; another is arsenic in coal. It occurs naturally in coal at an average concentration about the same as in the earth's crust. It also occurs naturally in the phosphates that are used in the manufacture of detergents.

AGRICULTURAL

Insecticides, fungicides, herbicides, and desiccants are widely used and are applied as sprays or dusts under many different conditions by aircraft and ground equipment. All the factors affecting the application have been discussed in the literature at great length; the droplet size, the spray drift, the fluid properties, the meteorological factors, the air movement, the nozzle types, the evaporation, and numerous other subjects.

There is a wealth of general information that has been published, but virtually none that is specific regarding the amount of spray or dust that is not effective. The pesticide industry as a whole merely answers that there are too many factors involved. A few documents have been located which contain some specific data relating to emissions that occur during cotton ginning operations.

The concentration of dust and arsenic observed near a cotton gin in Texas has been reported as shown in Table III, and the arsenic content of the particulate averages about 0.03 percent. Another study shows that the particulate discharged from ginning operations is 11.7 pounds per bale of cotton ginned [1]. Published statistics show that the production of cotton during 1968 was 10,948,000 bales (500 pounds per bale) [2].

ARSENIC EMISSIONS FROM COTTON GINNING

Cotton production 1968 (500 lb. bales)	10,948,000
Particulate discharge - lb/bale of cotton ginned	11.7
Arsenic content of particulate - percent	0.03

The particulate discharge was approximately 64,000 tons, and arsenic emissions were about 19 tons.

The burning of cotton gin trash is also known to be a source of arsenic emissions to the atmosphere. It has been reported that the trash averages about 700 pounds per bale of cotton produced

1- Air-borne Particulate Emissions from Cotton Ginning Operations; U. S. Public Health Service; Taft Engineering Center Technical Report A60-5; 1960.

2- Agricultural Statistics - 1969; U. S. Dept. of Agriculture.

TABLE III

SUSPENDED PARTICULATE AND ARSENIC CONCENTRATIONS IN THE AIR NEAR COTTON GINS IN WEST TEXAS - 1964 [1]

Distance from Gin (ft)	Range of Suspended Particulate Concentrations ($\mu g/m^3$)	Range of Arsenic Concentrations ($\mu g/m^3$)	Arsenic per μg Particulates Ratio x 10^4
150 - 300[a]	5,000 - 76,000	0.6 - 141	1.2 - 18.5
1,200 - 1,400[a]	385 - 187	.07 - 0.08	3.7 - 2.1
2,200 - 8,000[a]	217 - 42	.10 - 0.01	4.6 - 2.4
b	67 - 783		
Average			0.0003

a - Measurement downwind from the gin

b - Measurement upwind from the gin

1- Control and Disposal of Cotton-ginning Wastes; A Symposium; Public Health Service Publication 999-AP-31; May 3-4, 1966.

and that about 37 percent of the trash is burned [1]. Another report shows that arsenic lost from leaf trash during combustion averages about 76.6 percent [2]. Based on the assumption that the arsenic content of the trash is the same as that of the particulates emitted during ginning, calculations show 425 tons of arsenic in the trash burned, and 326 tons of arsenic emissions to the atmosphere.

There are many sources of arsenic emissions due to the use of pesticides other than those discussed above. There are emissions that occur during the application of sprays and dusts, the incineration of pesticide containers, and evaporation. In order to estimate these emissions, the problem was discussed with people knowledgeable with the application of pesticides. In most instances they were reluctant to estimate losses; however, a few did express an opinion. As a result, the atmospheric emissions of arsenic due to the use of pesticides during 1968 have been estimated at 3,270 tons, including 19 tons from cotton gins and 326 tons from burning cotton gin trash.

1- Control and Disposal of Cotton-ginning Wastes; A Symposium; Public Health Service Publication 999-AP-31; May 3-4, 1966.

2- Aboul-Ela, M. M. and Miller, C. S.; "Studies of Arsenic Acid Residues in Cotton"; Texas Agricultural Experiment Station; Texas A & M University; MP 771; June, 1965.

COAL

The arsenic content of various samples of coal has been reported as shown in Table IV, and the average concentration in domestic coal is about 5.44 ppm. Coal consumed in the United States during 1968 was 508,990,000 tons (bituminous and anthracite) [1]; therefore, the arsenic in coal was about 2,770 tons.

During combustion arsenic was discharged with the bottom ash and the fly ash. With respect to fly ash, a study has been made regarding emissions from coal fired power plants and the emissions of arsenic have been recorded. Arsenic concentrations in fly ash samples taken from the stack (after fly ash collection) ranged from 0.11 to 1.6 grains per scf x 10^{-4} [2]. Based on 508,990,000 tons of coal consumed, an arsenic concentration of 0.64 grains per scf x 10^{-4}, and 160 scf of flue gas per pound of coal, the arsenic emissions in the United States during 1968 due to the combustion of coal totaled 743 tons.

1- Minerals Yearbook; Bureau of Mines; 1968.

2- Cuffe, Stanley T. and Gerstle, Richard W.; "Emissions from Coal Fired Power Plants"; Public Health Service Publication No. 999-AP-35; 1967.

TABLE IV

AVERAGE ARSENIC CONTENT OF COAL ASH

Region	Frequency of Detection - %	As Content of Ash - %	Ash Content of Coal - %	As Content of Coal - %
Eastern Province	67	0.0107	9.3	0.000995
Interior Province	41	0.0049	10.5	0.000520
Western States	16	0.0012	9.8	0.000118
Average Arsenic Content in Coal				0.000544

NOTES - The above table based on "Spectrochemical Analyses of Coal Ash for Trace Elements"; Table 1; Bureau of Mines RI 7281; July 1969.

Averages were calculated for all samples tested using zero for arsenic contents below the limit of detection.

OIL

During this study numerous oil analyses were obtained that record the metal content of various crude and residual oils. Some of this information was obtained during a literature search, but most of it was unpublished data furnished by major oil companies and large users of residual oil. The data obtained included analyses of more than 400 samples of crude and residual oils from the Middle East, South America, and the United States. Most of the analyses showed the percent of vanadium, nickel, and copper, but not the arsenic content. Only one group of 110 tests of domestic crude oil included data concerning arsenic.

In 97 tests the arsenic was below the limit of detection, but in 13 tests the arsenic content ranged from 8 to 2,380 ppb. The average for the 110 tests was 42 ppb [1].

During 1968 the total new supply of oil in the United States was 4,922 million barrels [2]; about 79 percent was produced in the United States. Based on an average arsenic content of 42 ppb,

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1- Uranium and Other Metals in Crude Oils; Geological Survey Bulletin 1100; U. S. Government Printing Office; Washington, D. C.; 1961.

2- Crude Petroleum, Petroleum Products, and Natural Gas Liquids: 1968; Mineral Industry Surveys; Petroleum Statement; Annual.

the arsenic in the oil was about 36 tons; however, it is doubtful that this data is sufficiently accurate for estimating emissions. The arsenic content of imported residual oils is likely the most important factor not included in the above figures.

DETERGENTS

Arsenic has been detected in several common presoaks and household detergents that are marketed in the United States. The concentrations in various types are tabulated in Table V. It has been confirmed that the arsenic is not added intentionally; it occurs naturally in the phosphates that are used in the manufacture of the detergents.

Atmospheric emissions of arsenic that may occur due to use of detergents is considered as negligible.

PHOSPHORIC ACID

The phosphoric acid used for producing phosphates for foods, drugs, and detergents is normally made by the thermal process. Although the raw acid may contain arsenic, lead, and other heavy metals a very pure acid can be produced by treatment with a sulfide to precipitate the metal ions [1].

1- "Atmospheric Emissions from Thermal-Process Phosphoric Acid Manufacture"; Public Health Service Publication No. AP-48; 1968.

The phosphorus which is a basic raw material for the thermal process is usually made by reducing phosphate ore in electric furnaces. Therefore, it is likely that there are significant atmospheric emissions of arsenic during the production of phosphoric acid. The data to determine the magnitude of the emissions were not available during this study.

TABLE V

CONCENTRATIONS OF ARSENIC
IN CERTAIN DETERGENTS AND PRESOAKS [1]

	Detergent Type	Arsenic Concentration (ppm)	
		Average	Range
A.	EP	34	31-43
B.	HDED	32	SD
C.	HDD	9	8-10
D.	HDED	15	SD
E.	HDED	41	38-45
F.	EP	7	6-9
G.	DA	2	1-3*
H.	EP	59	51-73

*Lower limit of detection

NOTE: Abbreviations are:
EP - enzyme presoak
HDED - heavy duty enzyme detergent
DA - detergent aid
HDD - heavy duty detergent
SD - single determination

1- Angino, E. E., Magnuson, L. M., Waugh, T. C., Galle, O. K. and Bredfeldt, J.; "Arsenic in Detergents: Possible Danger and Pollution Hazard"; Science; 168; pp 389-390; Apr. 17, 1970.

INCINERATION AND OTHER DISPOSAL

Nearly all the uses of arsenic are such that very little remains for disposal. After it is used in pesticides, paint pigments, pyrotechnics, and many other products, a small amount remains in the shipping containers; in many instances this arsenic is disposed of by burning. The emissions resulting from this source have been included under Reprocessing and Consumptive Uses,

SEWAGE AND SLUDGE

A recent report concerning the burning of sewage and sludge indicates that the burning rate in the United States is about 2,000 tons per day, and the mercury content ranges up to 30 ppm [1]. The arsenic content is not stated.

Another report published in 1970 shows the arsenic concentration in the raw sewage input at a sewage treatment plant in Kansas to range from 2 to 3.4 ppb [2].

1- Private communication from the Federal Water Pollution Control Authority. (Investigations being conducted during 1971; therefore, data is subject to revision.)

2- Angino, E. E., Magnuson, L. M., Waugh, T. C., Galle, O. K. and Bredfeldt, J.; "Arsenic in Detergents: Possible Danger and Pollution Hazard"; Science; 168; pp 389-390; Apr. 17, 1970.

The arsenic content of the sewage burned in the United States was not available for this study, but it is believed that some arsenic is present in most sewage and that the concentration in sewage burned (dry) is considerably higher than in raw sewage. Arsenic emissions to the atmosphere due to the burning of sewage may be in the order of 2 to 10 tons per year.

IRON AND STEEL

During this study spectrographic analyses of dust samples from foundries have been examined; they all indicate arsenic and many other elements are contained in the dust. This information confirms that foundries, and possibly steel mills, are sources of arsenic emissions to the atmosphere.

The cupola is the most used method for producing cast iron. The rate of particulate emissions from gray iron cupolas has been reported as 4 to 26 pounds per ton of process weight not including emissions from handling, charging, or other non-melting operations.

Based on the information obtained from industry the particulate emission factor is estimated at 22 pounds per ton of process weight, including melting and non-melting operations. The

arsenic content of the particulate is about 0.07 percent [1]/ and the degree of emission control approximately 25 percent.

During 1968 the pig iron and scrap used by iron foundries totaled 16,788,000 short tons [2]/. Arsenic emissions to the atmosphere due to the production of cast iron were 97 tons.

1- Private communication with industrial source.

2- Minerals Yearbook; Bureau of Mines; 1968.

APPENDIX A

COMPANIES DEALING IN ARSENIC AND ARSENIC COMPOUNDS

CALIFORNIA	LOCATION
Electronic Space Products, Inc.	Los Angeles
DISTRICT OF COLUMBIA	
Hercules, Inc.	Washington
ILLINOIS	
Division Lead Company	Summit
MISSOURI	
Mallinckrodt Chemical Works	St. Louis
NEW JERSEY	
J. T. Baker Chemical Company	Phillipsburg
Rhodia, Inc.	New Brunswick
Sylvan Chemical Corporation	Englewood Cliffs
NEW YORK	
Alloys Unlimited, Inc.	Melville
American Smelting and Refining Co.	New York City
Anglo-American Metal & Ferro Alloy Corporation	New York City
Asarco Intermetallics Corporation	New York City
Ascher Alloys, Inc.	Brooklyn
Atomergic Chemetals Company	Carle Place, L. I.
Belmont Smelting and Refining Works	Brooklyn
City Chemical Corporation	New York City
Gallard-Schlesinger Chemicides, Inc.	Carle Place, L. I.
International Selling Corporation	New York City

Kawecki Chemical Company	New York City
McKesson Chemical Company	New York City
Mutchler Chemical Company, Inc.	New York City
Phillip Brothers Chemicals, Inc.	New York City
Republic Chemical Corporation	New York City
J. A. Samuel and Company, Inc.	New York City
Semi Alloys, Inc.	Mount Vernon
United Mineral & Chemicals, Inc.	New York City

OHIO

The Harshaw Chemical Company	Cleveland

PENNSYLVANIA

Bram Metallurgical Chemical Company	Philadelphia
The O. Hommel Company	Pittsburgh
Pennsylvania Coal Products Company	Petrolia
Rare Metal Products Company	Atglen
Semi-Elements, Inc.	Saxonburg

TEXAS

Industrial Materials Company	Houston

WASHINGTON

Cominco American Incorporated	Spokane

WISCONSIN

The Ansul Company	Marinette

(Thomas Register; Dec. 1968 Ed.)